ONR Technical Report RLT - 67

VISCOELASTIC PROPERTIES OF SOME ALKYL DISULFIDE COPOLYMERS

by

W. J. MacKnight, M. Takahashi and A. V. Tobolsky

(Contribution from the Frick Chemical Laboratory
Princeton University, Princeton, New Jersey)

December 1963

VISCOELASTIC PROPERTIES OF SOME ALKYL DISULFIDE COPOLYMERS

by

. J. MacKnight, M. Takahashi and A. V. Tobolsky

ABSTRACT

Modulus-temperature data, modulus-time data and glass transition temperatures have been obtained for the following copolymer systems:

    (1)   Ethylene disulfide and ethyl ether disulfide,

    (2)   Ethylene disulfide and ethyl formal disulfide,

    (3)   Ethylene disulfide and α paraxylene disulfide.

Master stress relaxation curves were constructed for poly(ethyl formal disulfide), poly(paraxylene disulfide) and poly(ethylene tetrasulfide) and show a marked resemblance to those obtained for amorphous hydrocarbon polymers.

VISCOELASTIC PROPERTIES OF SOME ALKYL DISULFIDE COPOLYMERS

by

W. J. MacKnight, M. Takahashi and A. V. Tobolsky

Introduction

Polysulfide polymers were the first synthetic rubbers produced in the United States and have been the subjects of many reviews and articles.[1-5] However, relatively little seems to have been published concerning the viscoelastic properties of these elastomers. The glass transition temperatures (T_g) of some of these substances have been measured[1] as have their cohesive energy densities,[2] dielectric constants and dipole moments,[3] and dynamic mechanical behavior.[4] Nevertheless, a systematic study of the viscoelastic behavior of polysulfides over a wide range of temperature and the relationship of this behavior to the structure of the polymers is lacking.

In the present study, copolymers of ethylene disulfide and ethyl ether disulfide ($-CH_2-CH_2-S_2$)/($-CH_2CH_2OCH_2CH_2S_2-$), ethylene disulfide and ethyl formal disulfide ($CH_2CH_2-S_2-$)/($CH_2CH_2OCH_2OCH_2CH_2S_2-$), and ethylene disulfide and α paraxylene disulfide ($CH_2CH_2-S_2-$)/($-CH_2-\langle O \rangle-CH_2-S_2-$) have been examined. These three copolymer series show systematic variations in their T_g's, their percentage crystallinity and their other viscoelastic properties depending on the particular co-monomers in their chain backbones and the amount of co-monomers present.

Experimental

The polysulfide copolymers were prepared by the interfacial polycondensation of mixtures of the appropriate dihalides (i.e., ethylene dichloride, bis 2 chloroethyl ether, bis 2 chloroethyl formal, and $\alpha\alpha'$dichloroparaxylene) and sodium disulfide of sulfur rank 2.16. The method is described in detail in references (1) and (6). In addition, the polymer latex was "toughened" by the addition of excess sodium polysulfide solution.[1] This insured the preparation of high molecular weight products. In all cases analysis corresponded quite closely to the theoretical quantities of the various components. It should be noted that the sulfur rank of the sodium polysulfide solution is the average of the various polysulfide ions present and that a distribution of species exists in the solution. This means that a polymer prepared from a sodium polysulfide solution of rank 2.16 contains mainly disulfide linkages but also contains some mono, tri and tetrasulfide linkages inter alia. Such a polymer is referred to as a disulfide polymer in this paper.

Polymer sheets were prepared by molding the rubber crumb in a hydraulic press.

Ten second torsion modulus measurements were made with a Gehman torsion tester.[7] Dow-Corning silicone fluid was used as a heat transfer medium. The rate of heating was

1°C per minute. Specific volume-temperature data were obtained by the displacement method of Wiley.[8] Methanol was used as the bath liquid. Volumes of the sample under study were calculated from the specific volume of methanol at each temperature. The temperature at which a sudden break in the specific volume-temperature curve occurred was taken to be the T_g of the polymer.

Stress relaxation master curves were constructed from isothermal modulus time curves made in a temperature range covering all regions of viscoelastic behavior.[16] The glassy region and the upper transition region were obtained using a Clash-Berg torsion tester.[9] The lower transition region and the rubbery region were obtained with a stress relaxation balance.[10] Tenney environmental equipment (model TSU 100-350) was used to achieve constant temperature. By adapting a bimetallic thermoregulator and a supersensitive relay, temperature control was accurate to $\pm$ 0.1°C.

The Clash-Berg apparatus gives the time dependent shear modulus, $G(t)$, while the stress relaxation balance yields the time dependent Young's modulus, $E_r(t)$. Since in the rubbery region $3G(t) \simeq E_r(t)$, $3G(t)$ has been used for the construction of the master curves.[17]

Results and Discussion

Figs. 1 through 3 are modulus temperature curves for the various homopolymers and copolymers studied. The

modulus plotted is the ten second shear modulus, $3G(10)$, and
the curves cover the glassy region, transition region and part
of the rubbery plateau region of viscoelastic behavior.[16]

The homopolymers exhibit wide variations in their
mechanical properties. Poly(ethyl ether disulfide) and poly
(ethyl formal disulfide) are amorphous polymers having low
T_i's (Table I). (T_i is defined as the temperature at which
$3G(10)$ is equal to 10^9 dynes cm^{-2}. This quantity is closely
related to the T_g of the polymer.)[16] Poly (paraxylene disul-
fide) is an amorphous polymer with a much higher T_i. (If poly
(paraxylene disulfide) is maintained at a temperature well
above its T_g for several days it crystallizes to a slight
extent.) Poly(ethylene disulfide), however, is highly crys-
talline. The modulus temperature curve for this polymer was
made by heating the sample above its melting point, quick
quenching it to the glassy state and measuring the modulus
as a function of temperature. Thus the indicated T_i for this
polymer is quite close to its T_g. The modulus temperature
curve shows the beginning of the transition region followed
by a sudden increase in modulus due to crystallization. The
modulus remains high until the melting point is reached when
the substance begins to flow.

Fig. 1 shows the modulus temperature curves for the
copolymer series based on ethylene disulfide and ethyl ether
disulfide. It is seen that the melting points and the degree

of crystallinity both decrease with increasing ethyl ether disulfide content as would be expected. Above an ethyl ether disulfide content of 40 mole percent the polymers are amorphous.

In the case of the ethyl formal disulfide-ethylene disulfide series (Fig. 2), the same phenomena are noted as with the ether series. However, in this case, the polymers become amorphous when the formal content becomes greater than twenty mole percent. This is probably due to the fact that the ethylformal disulfide does not "fit" into a crystal lattice as easily as ethyl ether disulfide and thus causes more disruption in the chain structure.

The α paraxylene disulfide ethylene disulfide series is shown in Fig. 3. In this case all the polymers have T_i's above that of pure poly(ethylene) disulfide. Further, all the polymers shown are amorphous. However, the compositions containing more than 80 mole percent of α paraxylene disulfide tend to crystallize to a slight extent if held well above their T_g's for a period of several days.

T_g Determinations

Values of T_i for all three copolymer series are given in Table I along with the T_g values for the formal and paraxylene series. Simha and Boyer[11] proposed that the expression $(\alpha_r - \alpha_g) T_g$ should be a constant for all amorphous polymers. In this expression α_r is the coefficient of expansion in the rubbery state and α_g is the coefficient of

expansion in the glassy state. T_g is in degrees K. The expression was evaluated for the formal and paraxylene series and is included in Table I.

Various empirical formulae have been proposed for predicting the T_g of an amorphous copolymer if the T_g's of both homopolymers are known. One of these empirical formulae which applies fairly well in many cases is:[12]

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \tag{1}$$

where w_1 and w_2 are the weight fractions of each of the components of the polymer, T_g is the glass transition temperature of the copolymer, T_{g_1} is the glass transition temperature of the homopolymer made up of one of the components of the copolymer and T_{g_2} is the glass transition temperature of the homopolymer made up of the other component of the copolymer.

In Fig. 5, eq. (1) is plotted together with the experimental T_g's and T_i's of the copolymer systems. The agreement is fairly good and thus eq. (1) should be useful for predicting the T_g of any copolymer composition in the systems studied.

Stress Relaxation Master Curves

Master curves for poly(ethyl formal disulfide), poly(paraxylene disulfide), and poly(ethylene tetrasulfide) are presented in Fig. 5. The reference temperatures for the

construction of these master curves were chosen to be close
to the T_i's of the polymers involved. Thus the shapes of the
three curves are quite similar. In all three cases, the
glassy, transition and rubbery plateau regions of viscoelastic
behavior are evident. In addition, the tetrasulfide polymer
shows the beginning of a flow region while no such behavior
appears with the disulfide polymers until much longer times.
One of the important characteristics of polysulfide elastomers
is their ability to undergo stress relaxation by the reversi-
ble interchange of the polysulfide linkages.[13] In the case
of the disulfides however, the special stability of the di-
sulfide bond[14] causes the relaxation to take place only by
the interchange of the small amount of higher polysulfide
linkages present along the chains.[15] As a result, the flow
region becomes apparent in the tetrasulfide polymer at much
shorter times than is the case with the disulfide polymers.

Since the tetrasulfide polymer flows by the mechan-
ism of bond interchange, the time-temperature superposition
principle would not be expected to apply to this region of
the polymer's viscoelastic behavior. This was indeed the case
as it was necessary to shift curves along both the abscissa
and the ordinate in order to superimpose them in this region.
For this reason, the flow region of the master curve is in-
dicated by a solid line on the graph.

The slopes of the linear sections of the master
curves, taken at $\log E_r(t) = 9.00$ are -0.61 for poly(ethyl

formal disulfide), -0.67 for poly(ethylene tetrasulfide) and -0.53 for poly(paraxylene disulfide). The Rouse-Bueche theory[18] gives a value of -0.5 for the slope while according to Zimm[19] the slope should be -0.67.

Application of a Modified Williams, Landel and Ferry Equation

The shift factors K(T), obtained by shifting the modulus time curves along the log time axis until they fit into a continuous curve were analyzed using the expression:

$$\log \frac{K(T)}{K(T_i)} \doteq -16.14 \frac{T - T_i}{56 + T - T_i} \tag{2}$$

where T_i is the characteristic temperature.

Equation (2) is of the form first proposed by Williams, Landel and Ferry and later slightly modified by Tobolsky and Catsiff.[21]

Fig. 6 is a plot of eq. (2) together with the experimental points for poly(ethyl formal disulfide), poly(ethylene tetrasulfide) and poly(paraxylene disulfide). A good fit is obtained for the region $-10 < T - T_i < 10$. At temperatures below $T_i - 10$, the polymers are well into the glassy region. The WLF equation was derived from the Doolittle viscosity equation [22, 23] which is based on the free volume concept. Below T_g there is presumably no further loss of free volume and thus application of eq. (2) is uncertain. At temperatures above $T_i + 10$, the agreement is particularly poor in the case of the tetrasulfide polymer. This is undoubtedly

due to the fact that in this region the mechanism of stress relaxation includes scission of polysulfide linkages as well as slippage of chain entanglements.

In conclusion it is interesting to note that the polymers studied exhibit viscoelastic behavior closely resembling that of hydrocarbon polymers. The master curves show a marked resemblance to those of polystyrene and polymethyl methacrylate.[17] This is worthy of note since the chain backbones of these substances contain large quantities of carbon-sulfur and sulfur-sulfur bonds which must differ greatly from normal carbon-carbon bonds.

Acknowledgement

References

1. Volume XIII, Part III in the series "High Polymers", Poly-alkylene Sulfides and other Polythioethers, N. G. Gaylord, ed., Interscience, New York, 1962, Chap. XIII, contains many references to the original literature.

2. Gee, G., Trans. Inst. Rubber Ind., $\underline{18}$, 266 (1943).

3. Kambura, S., J. Soc. Chem. Ind. Japan, $\underline{45}$, 1007 (1942).

4. Rorden, H. C. and A. Grieco, J. Applied Phys., $\underline{22}$, 842 (1951).

5. Patrick, J. C. and N. M. Mnookin, British Pat. 302, 270 (Dec. 13, 1927).

6. Tobolsky, A. V., R. B. Beevers and G. D. T. Owen, J. Colloid Sci., $\underline{18}$, 353 (1963).

7. ASTM Standards Designation D 1053-58 (1958).

8. Wiley, F. E., Ind. Eng. Chem., $\underline{34}$, 1052 (1942).

9. ASTM Standards Designation D 1043-51 (1958).

10. Tobolsky, A. V., "Properties and Structure of Polymers", John Wiley, New York, 1960, Sec. IV. 1 and Plate IV.

11. Simha, R. and R. F. Boyer, J. Chem. Phys., $\underline{37}$, 1003 (1962).

12. Fox, T. G., Bull. Am. Phys. Soc., $\underline{1}$, no. 3, 123 (1956).

13. Mochulsky, M. and A. V. Tobolsky, Ind. Eng. Chem., $\underline{40}$, 2155 (1948).

14. Owen, G. D. T., W. J. MacKnight and A. V. Tobolsky, J. Phys. Chem., In press.

15. Tobolsky, A. V., W. J. MacKnight and M. Takahashi, J. Phys. Chem., In press.

16. Tobolsky, A. V., "Properties and Structure of Polymers", John Wiley, New York, 1960, Sec. IV, 2.

17. Takahashi, M., M. Shen, R. B. Taylor and A. V. Tobolsky, J. Applied Polymer Sci., In press.

18. Bueche, F., J. Chem. Phys., $\underline{25}$, 599 (1956).

19. Zimm, B. H., J. Chem. Phys., $\underline{24}$, 269 (1956).

References (continued)

20. Williams, M. L., R. F. Landel and J. D. Ferry, J. Am. Chem. Soc., 77, 3701 (1955).

21. Tobolsky, A. V. and E. Catsiff, J. Polymer Sci., 19, 111 (1956).

22. Doolittle, A. K., J. Applied Phys., 22, 147 (1951).

23. Doolittle, A. K. and D. B. Doolittle, J. Applied Phys., 28, 901 (1957).
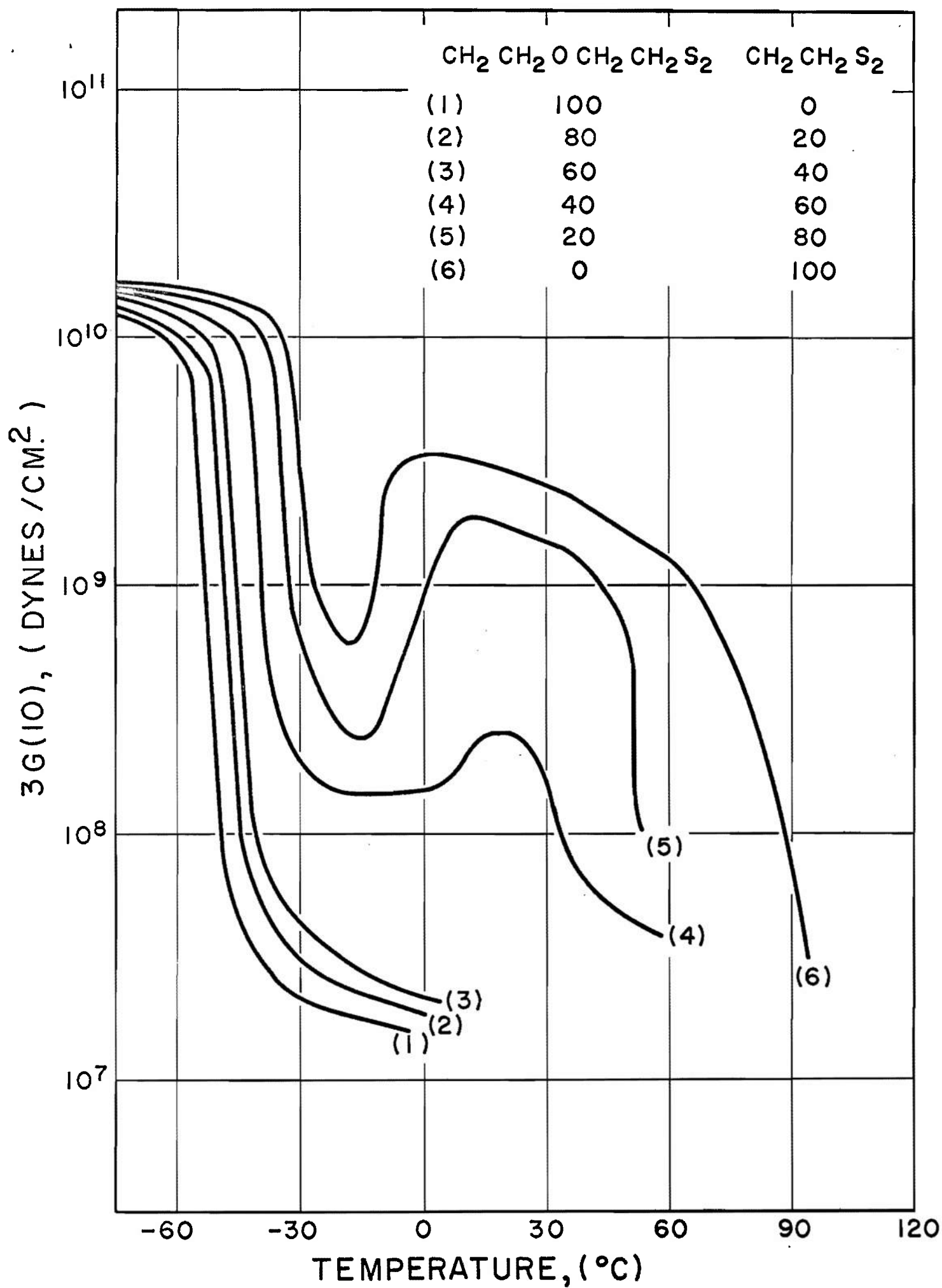
TABLE I

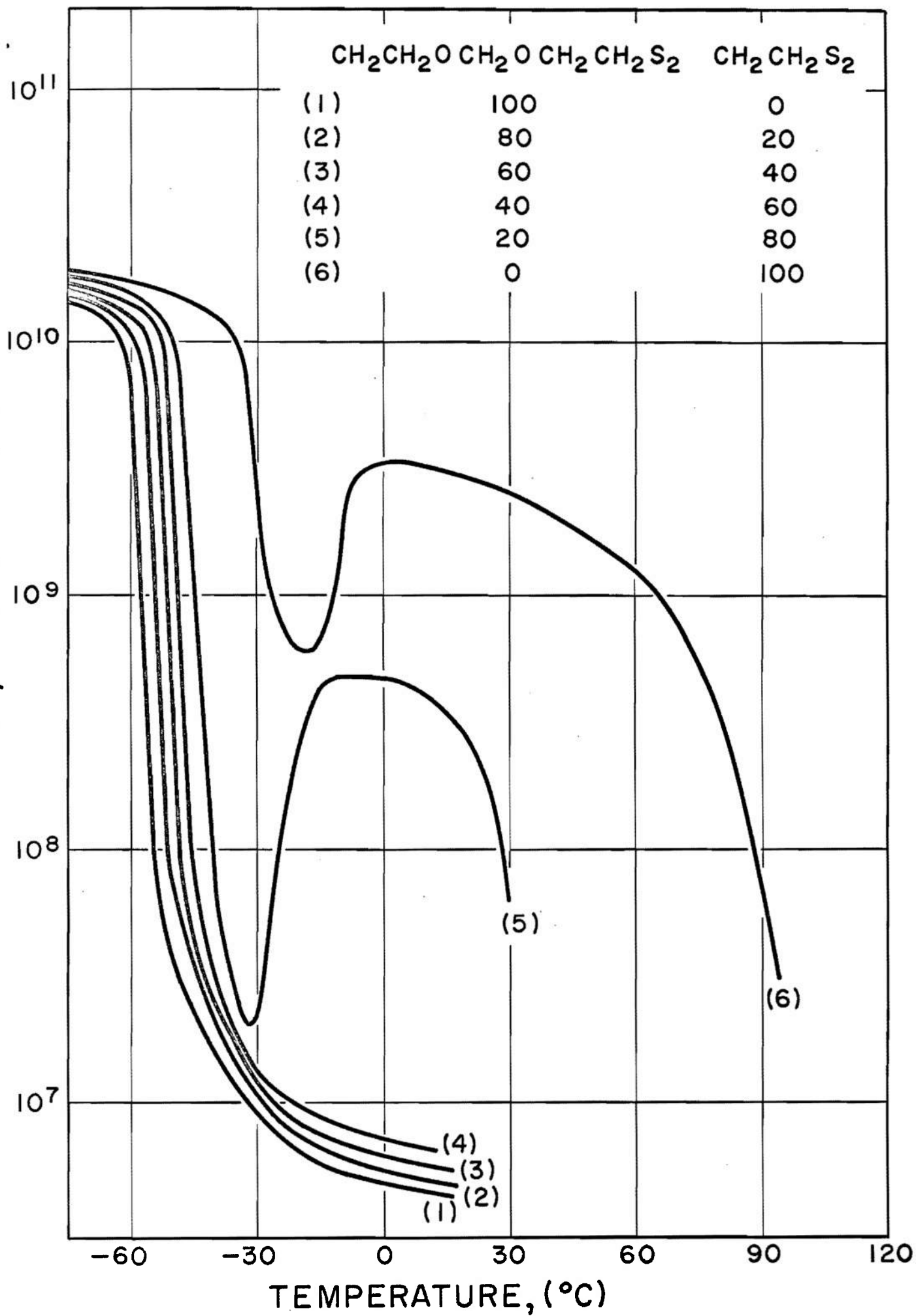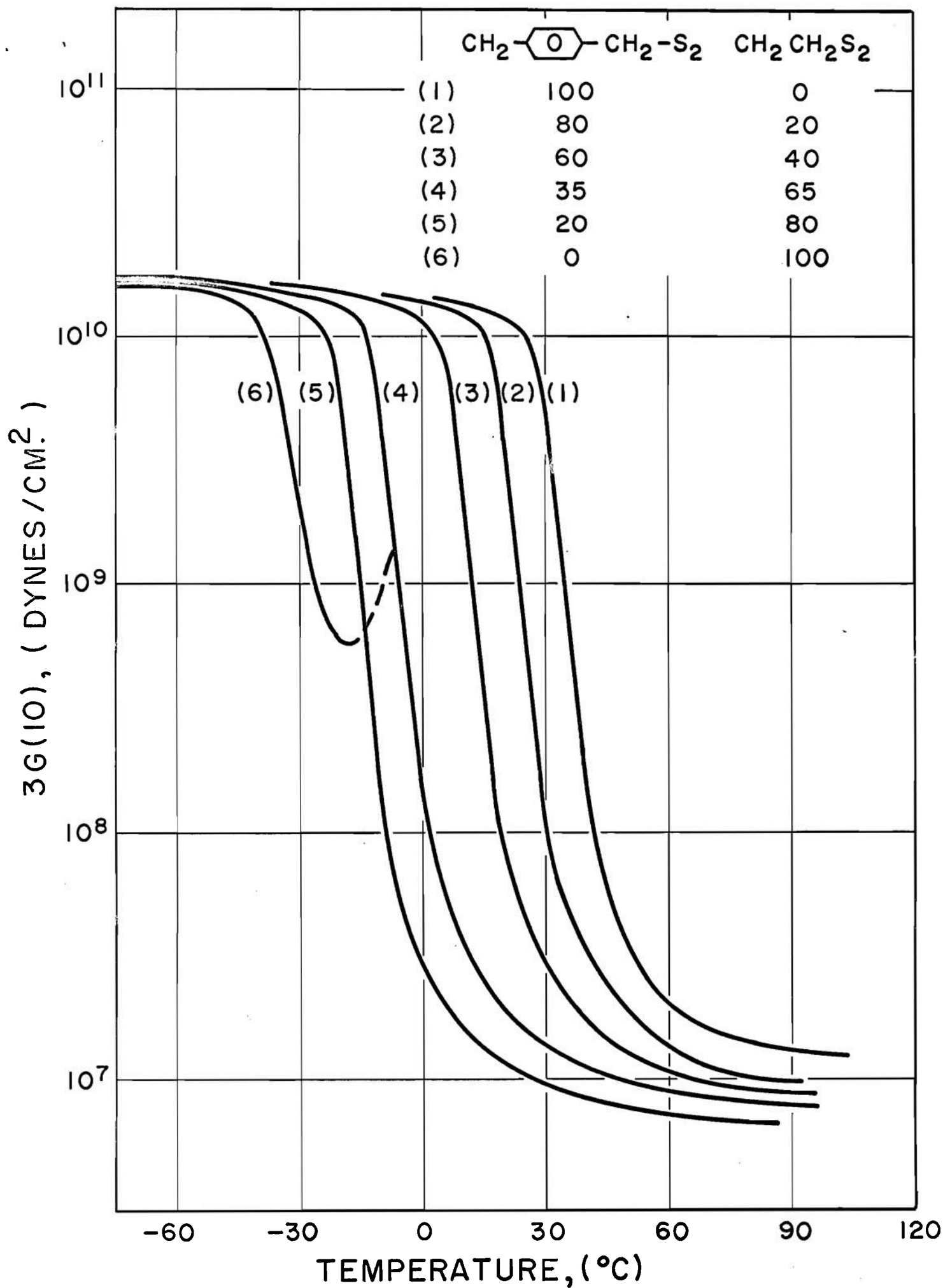|					T_i (°C)	T_g (°C)	$(r-g)$
100	$CH_2\langle O \rangle CH_2S_2$	0	$CH_2.CH_2.S_2$	C	34	21	.0844
80		20		C	22	14	.0788
60		40		A	11	5	.0870
35		65		A	-6	-10	.0779
20		80		A	-16	-18	.0732
00		100		C	-27	-27	---
100	$CH_2.CH_2.O.CH_2.CH_2.S_2$	0	$CH_2.CH_2.S_2$	A	-53		
80		20		A	-49		
60		40		A	-46		
40		60		A	-38		
20		80		A	-32		
100	$CH_2.CH_2.OCH_2.OCH_2CH_2S_2$	0	$CH_2.CH_2S_2$	A	-58	-59	.0750
80		20		A	-55	-56	.0784
60		40		A	-52	-53	.0530
40		60		A	-49	--	
20		80		C	-45	-46	.0605

A: Amorphous   C: Crystalline

Captions for Figures
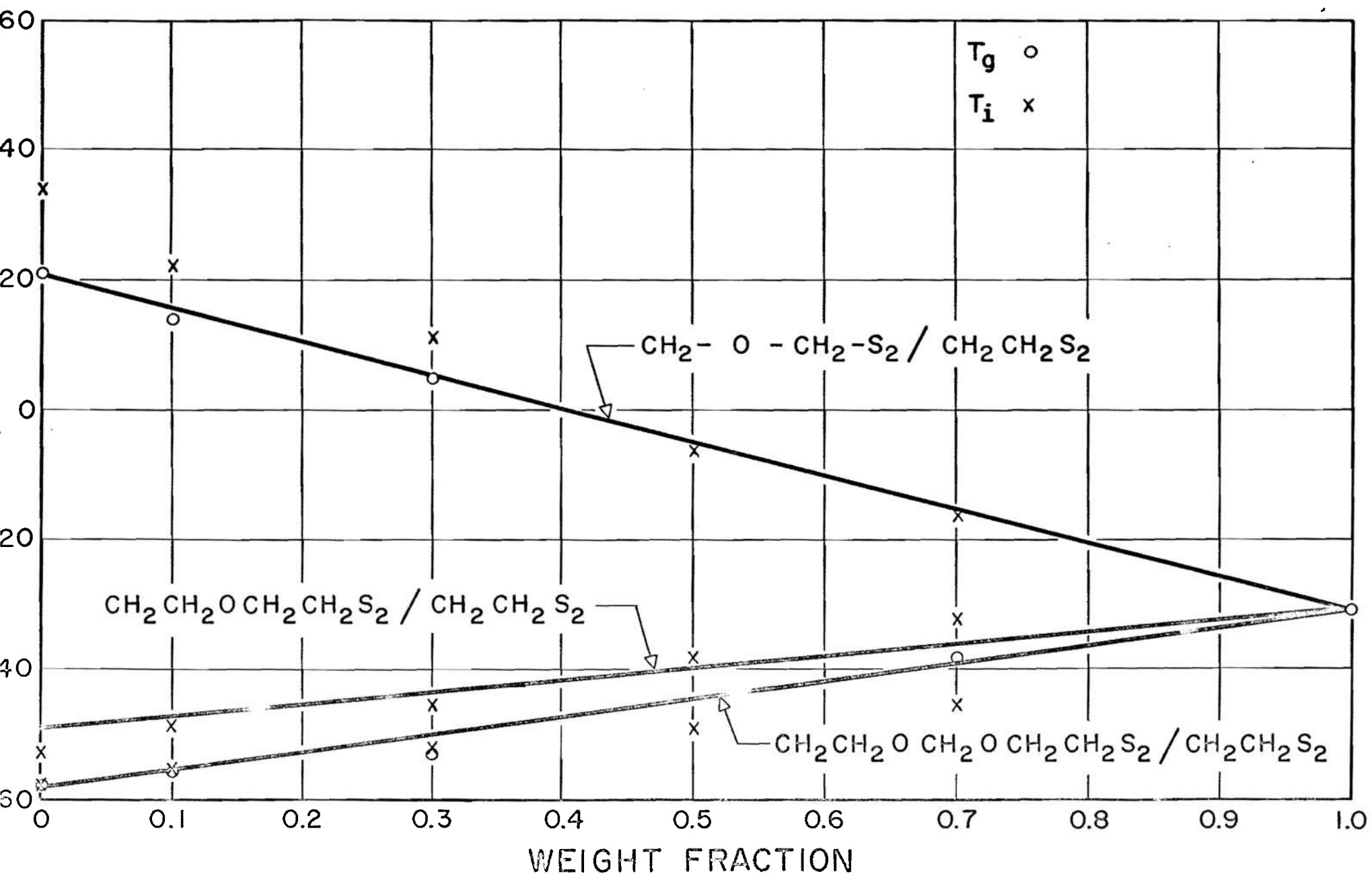
Fig. 1.   Modulus temperature curves for copolymers
        of ethyl ether disulfide and ethylene disulfide.

Fig. 2.   Modulus temperature curves for copolymers
        of ethyl formal disulfide and ethylene disulfide.

Fig. 3.   Modulus temperature curves for copolymers
        of $\propto$ paraxylene disulfide and ethylene disulfide.

Fig. 4. T_g and T_i versus weight fraction for copolymers
        of ethyl ether disulfide and ethylene disulfide;
        of ethyl formal disulfide and ethylene disulfide and
        of $\propto$ paraxylene disulfide and ethylene disulfide.

Fig. 5.   Stress relaxation master curves
        for poly(ethyl formal disulfide) Ref. Temp. = -60°C;
        for poly(ethylene tetrasulfide) Ref. Temp. = -19°C; an
        for poly(paraxylene disulfide) Ref. Temp. = 36oC.

Fig. 6.   WLF equation for poly(ethyl formal disulfide), poly
        (paraxylene disulfide) and poly(ethylene tetrasulfide).
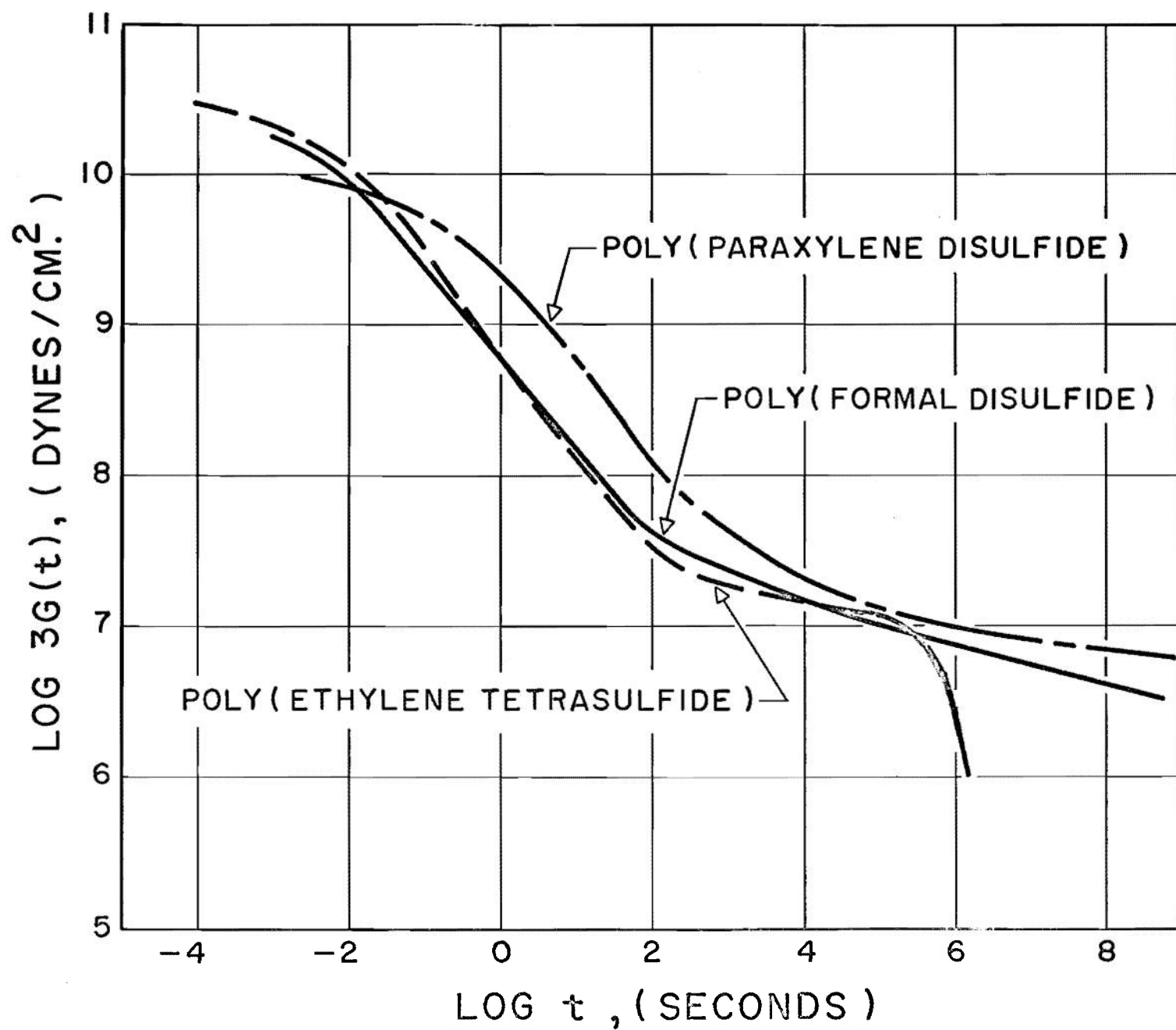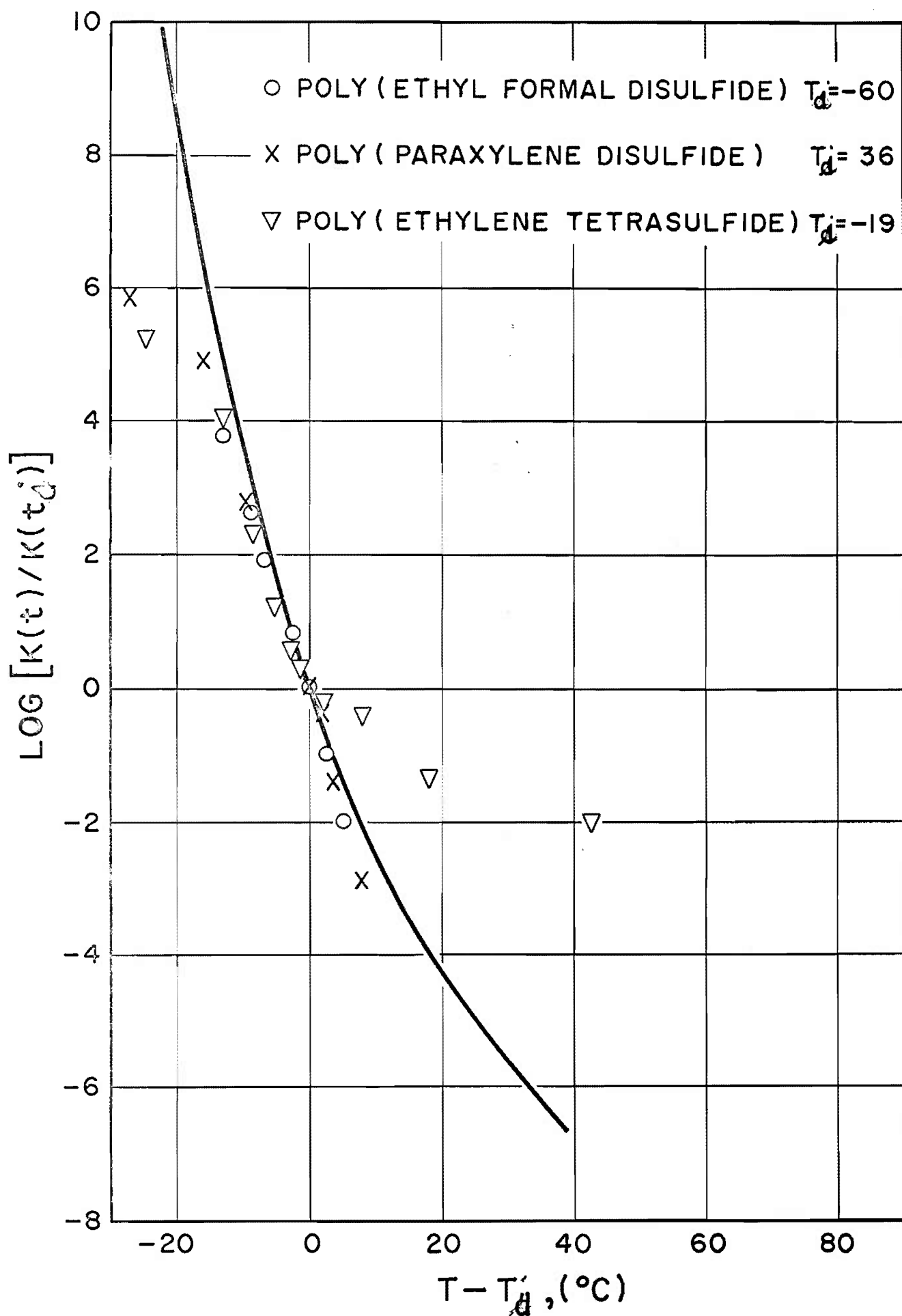
Plot of $\mathrm{LOG}\left[\kappa(t)/\kappa(t_G')\right]$ versus $T-T_d'$, $(\degree C)$

Legend:
- ○ POLY(ETHYL FORMAL DISULFIDE) $T_d' = -60$
- × POLY(PARAXYLENE DISULFIDE) $T_d' = 36$
- ▽ POLY(ETHYLENE TETRASULFIDE) $T_d' = -19$

Contract Number - Nonr 1858(07)   NR No. 356-377

Commanding Officer
Office of Naval Research Branch Office
230 N. Michigan Avenue
Chicago 1, Illinois   (1)

Commanding Officer
Office of Naval Research Branch Office
207 West 24th Street
New York 11, New York   (1)

Commanding Officer
Office of Naval Research Branch Office
1030 East Green Street
Pasadena 1, California   (1)

Commanding Officer
Office of Naval Research Branch Office
Box 39, Navy No. 100, F.P.O.
New York, New York   (7)

Director, Naval Research Laboratory
Washington 25, D. C.
Attn: Technical Information Officer   (6)
       Chemistry Division   (2)

Chief of Naval Research
Department of the Navy
Washington 25, D. C.
Attn: Code 425   (2)
       Code 468   (1)

DDR and E
Technical Library
Room 3C-128, The Pentagon
Washington 25, D. C.   (1)

Department of the Army
Supply and Maintenance Command
Maintenance Readiness Division
Washington 25, D. C.
Attn: Technical Director   (1)

U.S. Army Natick Laboratories
Clothing and Organic Materials Division
Natick, Massachusetts
Attn: Associate Director   (1)

Harry Diamond Laboratories
Washington 25, D. C.
Attn: Library   (1)

Office, Chief of Research and Development
Department of the Army
Washington 25, D. C.
Attn: Physical Sciences Division   (1)

Chief, Bureau of Ships
Department of the Navy
Washington 25, D. C.
Attn: Code 342A   (2)

Technical Library, DLI-3
Bureau of Naval Weapons
Department of the Navy
Washington 25, D. C.   (4)

Defense Documentation Center
Cameron Station
Alexandria, Virginia   (20)

Commanding Officer
U.S. Army Electronics Research and
   Development Laboratory
Attn: SELRA/DR
Fort Monmouth, New Jersey 07703   (1)

Naval Radiological Defense Laboratory
San Francisco 24, California
Attn: Technical Library   (1)

Naval Ordnance Test Station
China Lake, California
Attn: Head, Chemistry Division   (1)
       Code 40   (1)
       Code 50   (1)
Commanding Officer
Army Research Office
Box CM, Duke Station
Durham, North Carolina
Attn: CRD-AA-UO   (1)

Atomic Energy Commission
Division of Research
Chemistry Programs
Washington 25, D. C.   (1)

Atomic Energy Commission
Division of Technical Information
   Extension
Post Office Box 62
Oak Ridge, Tennessee   (1)

Commanding Officer
U.S. Army Chemical Research and
   Development Laboratories
Attn: Librarian
Edgewood Arsenal, Maryland   (1)

Dr. P. A. Miller
ONR Branch Office
1000 Geary Street
San Francisco 9, California   (1)

Contract Number · Nonr 1858(07)

ONR Resident Representative
James Forrestal Research Center
Princeton University
Princeton, New Jersey   (1)

Dr. Albert Lightbody
Naval Ordnance Laboratory
White Oak, Silver Spring, Maryland   (1)

Dr. A. Eisenberg
Department of Chemistry
University of California
Los Angeles, California   (1)

Dr. W. H. Avery
Applied Physics Laboratory
The Johns Hopkins University
8621 Georgia Avenue
Silver Spring, Maryland   (1)

Dr. J. H. Faull, Jr.
72 Fresh Pond Lane
Cambridge 38, Massachusetts   (1)

Chief, Bureau of Yards and Docks
Department of the Navy
Washington 25, D. C.
Attn: Code P300   (1)

Aeronautical Systems Division
ASRCNP
Wright-Patterson AFB, Ohio   (1)

Office of Chief of Engineers
Research and Development Division
Department of the Army
Gravelly Point
Washington 25, D. C.   (1)

Engineers Research and Development Lab.
Fort Belvoir, Virginia
Attn: Materials Branch, Mr. Mitton   (1)

Commander Mare Island Naval Shipyard
Rubber Laboratory
Vallejo, California   (1)

Aerojet-General Corporation
Azusa, California
Attn: Technical Library   (1)

Commanding Officer
Picatinny Arsenal
Dover, New Jersey
Attn: ORDTB   (1)

Dr. R. S. Stein
Organics Division
Olin Mathieson Chemical Corporation
275 Winchester Avenue
New Haven, Connecticut   (1)

Mr. W. M. Lee, Director
Contract Research Department
Pennsalt Chemicals Corporation
900 First Avenue
King of Prussia, Pennsylvania   (2)

Commanding Officer
Naval Air Development Center
Johnsville, Pennsylvania
Attn: Dr. Howard R. Moore   (1)

Plastics Technical Evaluation Center
Picatinny Arsenal
Dover, New Jersey   (1)

NASA
1512 H Street, N.W.
Washington 25, D. C.   (1)

Dr. B. Wunderlich
Department of Chemistry
Rensselaer Polytechnic Institute
Troy, New York   (1)

Monsanto Research Corporation
Everett Station
Boston 49, Massachusetts
Attn: Librarian   (1)

Commanding Officer
Ordnance Materials Research Office
Watertown Arsenal
Watertown 72, Massachusetts
Attn: RPD   (1)

Commanding Officer
Rock Island Arsenal
Rock Island, Illinois
Attn: Mr. R. Shaw, Laboratory   (1)

Dr. M. S. Cohen, Chief
Propellants Synthesis Section
Reaction Motors Division
Denville, New Jersey   (1)

Dr. T. G. Fox, Director
Mellon Institute
4400 Fifth Avenue
Pittsburgh 13, Pennsylvania   (1)

Contract Number - Nonr 1858(07)

Dr. M. E. Kenney
Department of Chemistry
Case Institute of Technology
Cleveland, Ohio (1)

Mr. J. A. Kies
Code 6210
Naval Research Laboratory
Washington 25, D. C. (1)

Dr. R. S. Nyholm
University College London
London, England **(1)**

Dr. R. B. Fox **(1)**
Mr. J. E. Cowling (1)
Dr. A. L. Alexander (1)
Dr. D. L. Venezky (1)
Code 6120
Naval Research Laboratory
Washington 25, D. C.

Mr. E. J. Kohn
Code 6110
Naval Research Laboratory
Washington 25, D. C. (1)

New York Naval Shipyard
Material Laboratory
Brooklyn 1, New York
Attn: Mr. B. B. Simms (1)

Frost Engineering Development Corporation
3946 South Broadway
Englewood, Colorado (1)

Commanding Officer
Rock Island Arsenal
Rock Island, Illinois (1)

Director, National Bureau of Standards
Washington 25, D.C.
Attn: Chief, Organic and Fibrous
Materials Division (1)

Dr. L. F. Rahm
Plastics Laboratory
Princeton University
Princeton, N.J. (1)

Dr. W. Heller
Department of Chemistry
Wayne State University
Detroit, Michigan (1)

Dr. U. P. Strauss
Department of Chemistry
Rutgers - The State University
New Brunswick, New Jersey (1)

Dr. E. G. Rochow
Department of Chemistry
Harvard University
Cambridge 38, Massachusetts (1)

Prevention of Deterioration Center
National Research Council
2101 Constitution Avenue, N.W.
Washington 25, D.C. (1)

Mr. H. D. Moran
Aircraft Industries Association
7660 Beverly Boulevard
Los Angeles 36, California (10)

Dr. T. L. Heying
Organics Division
Olin Mathieson Chemical Corporation
275 Winchester Avenue
New Haven, Connecticut (1)

Dr. M. S. Cohen, Chief
Propellants Synthesis Section
Reaction Motors Division
Denville, New Jersey (1)